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Natural transformation of chlordecone into 5b-hydrochlordecone in French West Indies soils: statistical evidence for investigating long-term persistence of organic pollutants

Damien A. Devault[1,2] · **Christophe Laplanche**[3] · **Hélène Pascaline**[1] · **Sébastien Bristeau**[4] · **Christophe Mouvet**[5] · **Hervé Macarie**[6,7]

Abstract Chlordecone (CLD) was an organochlorine insecticide whose previous use resulted in an extensive pollution of the environment with severe health effects and social consequences. A closely related compound, 5b-hydrochlordecone (5b-hydroCLD), has been searched for and often detected in environmental matrices from the geographical area where CLD was applied. The current consensus considered that its presence was not the result of a biotic or abiotic dechlorination of CLD in these matrices but rather the consequence of its presence as impurity (synthesis by-product) in the CLD released into the environment. The aim of the present study was to determine if and to what extent degradation of CLD into 5b-hydroCLD occurred in the field. To test this hypothesis, the ratios of 5b-hydroCLD and CLD concentrations in a dataset of 810 soils collected between 2006 and 2012 in Martinique were compared to the ratios measured in 3 samples of the CLD dust commercial formulations applied in the banana fields of French West Indies (FWI) and 1 sample of the technical-grade CLD corresponding to the active ingredient used in such formulations. Soil data were processed with a hierarchical Bayesian model to account for random measurement errors and data censoring. Any pathway of CLD transformation into 5b-hydroCLD occurring over the long term in FWI soils would indeed change the ratio of 5b-hydroCLD/CLD compared to what it was in the initially applied formulations. Results showed a significant increase of the 5b-hydroCLD/CLD ratio in the soils—25 times greater in soil than in commercial formulations—which suggested that natural CLD transformation into 5b-hydroCLD over the long term occurred in these soils. Results from this study may impact future decisions for the remediation of the polluted areas.

✉ Damien A. Devault
damien.devault@martinique.univ-ag.fr

[1] EA 929 AIHP-GEODE, Groupe Biospheres, Université des Antilles, Campus de Schœlcher, Schœlcher Cedex, France

[2] Faculté de Pharmacie, UMR 8079, CNRS AgroParisTech, Univ. Paris Sud, 75005 Paris, France

[3] INP, UPS, CNRS, ECOLAB (Laboratoire Ecologie Fonctionnelle et Environnement), ENSAT, Université de Toulouse, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

[4] Division Laboratoires, BRGM, 3 Avenue Claude Guillemin, BP6009, 45060 Orléans Cedex, France

[5] Division Eau, Environnement et Ecotechnologies, BRGM, 3 avenue Claude Guillemin, BP6009, 45060 Orléans Cedex, France

[6] IRD, UMR IMBE, Campus Agro-environnemental Caraïbe, BP 214, 97285 Lamentin, France

[7] Aix Marseille Université, CNRS, IRD, Avignon Université, IMBE, UMR 7263 – IRD 237, 13397 Marseille, France

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Introduction

Anthropogenic contamination of ecosystems by pesticides has become a major environmental and sanitary concern. The impact of these products on human health and ecosystem integrity is a known fact, especially for persistent ones (Bro-Rasmussen 1996). Ecosystem contamination resulting from agricultural practices has been the subject of many studies, but for the most persistent organic pollutant (POP) field or laboratory metabolism studies are hindered by the very long half-lives of the compounds studied. The environmental management of the impact of such compounds is driven by the POP half-life, i.e. depending on the persistence and concentration of POP, the land remediation could be expected at enough short term for developing waiting solutions (temporary diversification or fishermen subvention) or not, leading to a ban of every use critically impacted by considered pollution. Such a conflict of alternatives is involved in the case of chlordecone in the French West Indies (FWI) (Dubuisson et al. 2007).

Chlordecone[1] (CLD) was an organochlorine insecticide applied to fight weevil (*Cosmopolites sordidus*) infestations of banana plantations between the years 1972 and 1978 and then 1981 to 1993 in the FWI. It was used under the form of a dust formulated at 5 % CLD by weight with talc as diluting material. The CLD commercial formulations originated from the USA for the first period of application and Brazil (active ingredient)/France (final diluted product) for the second period and were sold under the trade names Kepone® and Curlone®, respectively. CLD has also been used in Europe, the USA, Africa, and Latin America (Le Déaut and Procaccia 2009). Among the total of 1800 t of CLD produced over time in the world, one sixth was spread in Martinique and Guadeloupe (but to a lesser extent in that second case) (Le Déaut and Procaccia 2009). This led to severe contamination of soils (Cabidoche et al. 2009), surface waters and groundwater (respectively, Bocquené and Franco 2005 and Gourcy et al. 2009), plant products (Cabidoche and Lesueur-Jannoyer 2012), fresh water and seafood (Coat et al. 2006 and 2011), and livestock (e.g. Jondreville et al. 2014) and wildlife (Cavelier 1980). Other organochlorine insecticides, with chemical structures similar to CLD, have been used worldwide, e.g. Mirex[2] and Kelevan.[3] In Europe, Kelevan (an adduct between CLD and levulinate) was used against the Colorado potato beetle (*Leptinotarsa decemlineata*) (Maier-Bode 1976; Galuszka et al. 2011). It was known to convert rapidly into CLD in soils (Maier-Bode 1976). Besides its use as an insecticide, Mirex was also used as a flame retardant, and this resulted in considerable public notoriety (Kaiser 1978; Hodgson 1998). This led to its inclusion in the first 'dirty dozen' list of POPs with its use and production controlled under the Stockholm international treaty (e.g. Mrema et al. 2013; Stockholm convention website 2015). Mirex was expected to oxidize to CLD by photolysis (Ivie et al. 1974; Carlson et al. 1976). Contamination by CLD was reported in French Polynesia for coral fish (Roche et al. 2011) and in whitespotted bamboo shark (*Chiloscyllium plagiosum*), fished near Hong Kong (Cornish et al. 2007). The presence of CLD in these locations where CLD direct use has never been documented could be related to the spread of the other pesticides Kelevan and Mirex considering their aforesaid ability to transform into CLD under environmental conditions. As such, the environmental and sanitary concerns associated to CLD may have a much wider geographical range than initially thought.

The acute sanitary, environmental, economic and social impact of CLD pollution in the FWI led to limitations or bans on economic and traditional activities deeply rooted in FWI populations like fishing, tuber cultivation and kitchen gardening (Joly 2010).

The sanitary impact on the local population notably includes increased risk of the occurrence of prostate cancer (Multigner et al. 2010), negative effects on cognitive and motor development of 7-month-old infants (Dallaire et al. 2012), and increased risk of preterm birth (Kadhel et al. 2014).

Environment contamination due to CLD presents two main characteristics: ubiquity (Houdart et al. 2009) and apparent in situ non-degradability of the CLD (Huggett 1989; Cabidoche et al. 2009). The resulting apparent lack of natural remediation impacted the governance and social perception of the issue raised by CLD contamination. However, according to the theoretical study performed by Dolfing et al. (2012), there should be no thermodynamic restriction to the ultimate biological mineralization of CLD under a wide range of redox conditions (O_2, Fe^{3+}, NO_3^-, SO_4^{2-} and CO_2 as main electron acceptors; Dolfing et al. 2012). Its partial transformation by reductive dechlorination should be also possible but probably restricted

[1] CAS name: 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one

[2] CAS name: dodecachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalene

[3] CAS name: 1,3,4-metheno-1*H*-cylobuta[*cd*]pentalene-2-pentanoic acid, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-2-hydroxy-γ-oxo-ethyl ester

to (or at least favoured in) anaerobic environments rich in labile organic matter as electron donor for the process (Dolfing et al. 2012). Such conditions do not correspond to the situation in the FWI for soils used to grow bananas (andosol, ferralsol and nitisol) that are too draining for allowing anaerobiosis. In the case of andosol (corresponding to around 49 % of the surface covered by banana crops in Martinique), this restriction is doubled by the fact that its abundant organic matter (1 to 13 % carbon *w*/*w*) is well known to be very little biodegradable and so corresponds to a poor electron donor (e.g. Chevallier et al. 2010). Incubation of FWI andosols spiked with ^{14}C-CLD under aerobic conditions (similar to most field situations in FWI) over a period of 7 months has recently confirmed their very low capacity to mineralize (less than 3–5 % of ^{14}C-CLD recovered as $^{14}C\text{-}CO_2$ and with $^{14}C\text{-}CO_2$ production rate decreasing over time and almost nil at the end) or to partially transform (no metabolites detected) CLD (Fernández-Bayo et al. 2013). By contrast, the test of the "in situ chemical reduction" (ISCR) remediation process involving the addition of a mixture of micrometric Fe° and grounded dried alfalfa to soil at the laboratory scale with actual FWI soils resulted in the case of ferralsol and nitisol in up to 74 % of CLD transformation and identification of 14 dechlorinated transformation products (Mouvet et al. 2012).

5b-Hydrochlordecone[4] (5b-hydroCLD), whose structure is identical to CLD except that one chlorine atom is replaced by a hydrogen at position 5b (Chemical Abstracts Service (CAS) numbering) and which is commercially available as an analytical standard, has been searched for and often detected in environmental matrices (soil, surface water and groundwater, sediments, plants, avian tissues and eggs, crustaceans, molluscs and fishes) from the geographical areas where CLD was applied (FWI) or unintentionally released during its manufacture (USA) (Borsetti and Roach 1978; Harless et al. 1978; Stafford et al. 1978; Carver and Griffith 1979; Orndorff and Colwell 1980; Coat et al. 2011; Martin-Laurent et al. 2014; Clostre et al. 2014a, b). The current tacit assumption is that the presence of this compound is not the result of a biotic or abiotic dechlorination of CLD in these matrices but rather the consequence of its presence as an impurity, a by-product of its preparation, in the CLD released in the environment (Borsetti and Roach 1978; Cabidoche et al. 2009; Coat et al. 2011; Martin-Laurent et al. 2014). Until now, however, this assumption could not be verified since no detailed chemical analyses of the CLD commercial formulations (and so of their 5b-hydroCLD content) seem to exist in the literature.

The aim of the present study was to determine whether—and if yes to what extent—degradation of CLD into 5b-hydroCLD occurs in the field. To test this hypothesis, the ratios of 5b-hydroCLD and CLD concentrations in a dataset of 810 soils collected between 2006 and 2012 (737 soils from sampling campaigns performed by the Direction de l'Agriculture, de l'Alimentation et de la Forêt, DAAF 972—Agriculture, Food and Forest Agency of Martinique—and 73 from the Bureau de Recherches Géologiques et Minières (BRGM); French geological survey) were compared to the ratios measured in 3 samples of Curlone® commercial formulations and 1 sample of technical-grade Kepone®, the active ingredient diluted to produce the 5 % Kepone®, that were used when CLD was applied in the banana fields of FWI. Data were processed in two steps, using standard statistical procedures first, followed by a more advanced hierarchical Bayesian modelling which accounts for errors in the measurement and sampling processes.

The detailed discussion that follows provides reasons and possible pitfalls answering the reasons behind the observed differences of 5b-hydroCLD/CLD mass ratios in soils and in initially applied formulations.

Materials and methods

Sampling of soils and CLD commercial formulations

DAAF 972 and BRGM soils

Soils were sampled from the 0–30-cm layer with an auger. The sampling strategy was specifically developed for the evaluation of soil contamination by CLD, whose spreading on banana roots led to a rosette-shaped soil contamination (Clostre et al. 2014a). Briefly, a three-point triangle-shaped sampling was performed to be representative of soil contamination, considering the banana tree spacing. The samplings were performed by technicians of DAAF 972 and BRGM.

CLD commercial formulations

Detailed information (geographical origin, name of manufacturers, dates of formulation, sampling and chemical analysis) for the Kepone® technical grade and the three Curlone® samples that could be retrieved is given in Table 1. The samples will be thereafter referred as Kepone-VIMS, Curlone-Cirad, Curlone-IRD and Curlone-UAG according to the names of the institutions that provided them. No additional samples could be found due to the fact that the existing Curlone® stocks were actively collected and destroyed after the ban of CLD use by the French authorities in 1993.

[4] CAS name 1,1a,3,3a,4,5,5,5a,5b-nonachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one

Table 1 Origin of the Curlone® and technical-grade Kepone® samples analyzed in this study, together with their content of CLD and 5b-hydroCLD

Sample identification	Geographical origin	Producer	Date of formulation	Date of sampling	Date of analysis	Concentration of compounds in samples (mass % of raw material)[a]	
						CLD	5b-HydroCLD
Curlone-UAG	Guadeloupe	Laurent de Lagarrigue S.A.	Sept. 1983	March 2012	Nov. 2012	4.26±0.19	0.0035±0.0002
Curlone-Cirad	Guadeloupe	Laurent de Lagarrigue S.A	Unknown	2004	Nov. 2012	4.23±0.27	0.0032±0.00007
Curlone-IRD	Martinique	Laurent de Lagarrigue S.A.	Sept. 1983	July2012	Nov. 2012	4.76±0.37	0.0033±0.0002
Kepone-VIMS	Virginia, USA	Allied Chemicals	Before 1976	May2012	Nov. 2012	71.9±8.28	0.0491±0.007

[a] Values after '±' correspond to standard deviation

Chemical analysis of soils and commercial formulations

Chemical analysis of DAAF 972 soils

Analyses of DAAF 972 soils were performed by the French public analysis laboratory of Drôme (LDA26), after sample storage and expedition from Martinique by equivalent local laboratory (LDA972). Accelerated solvent extraction (ASE) of air-dried samples was carried out with dichloromethane and acetone (50:50 *v*/*v*). After concentration and purification, CLD and 5b-hydroCLD content was quantified by GC-ECD with a VARIAN (Palo Alto, CA, USA) GC 3800 and/or by GC–MS/MS with a VARIAN GC 450 and MS 240. To ensure CLD and 5b-hydroCLD identification, three transitions from precursor ion m/z 272 were monitored: m/z 235, 237 and 239 (excitation storage level m/z 74.9 and excitation amplitude 1.6 V). For confirmation, m/z 237 was used as quantifier and m/z 235 (25 %) and 239 (15 %) as qualifiers. Extraction efficiency and quantification were validated using the standard addition method and surrogate compounds hexabromobenzene and triphenyl phosphate that were added to soil samples before extraction (source of products LGC Promochem). Extraction yield was measured on 119 soil samples for CLD and 30 soil samples for 5b-hydroCLD. Mean extraction yield was 83 % for CLD and 68 % for 5b-hydroCLD (Félix Massat, LDA26 Head, personal communication). The CLD and 5b-hydroCLD limit of quantification (LOQ) was 0.01 mg/kg soil dry weight (dw). Several operators handled the chemical analysis of CLD and 5b-hydroCLD in soil samples. Depending on the operator, CLD and 5b-hydroCLD were rounded (or not) to the nearest 0.01 mg/kg soil dw.

Chemical analysis of BRGM soils and CLD commercial formulations

The BRGM soils and CLD formulations were analyzed by BRGM following a protocol published elsewhere (Bristeau et al. 2014). Briefly, 5 g of soil or 0.1 g of Curlone® or 0.01 g of Kepone-VIMS was placed in a 22-mL cell with at the bottom a cellulose paper disc, completed by Hydromatrix (to remove moisture), then extracted with an ASE 350 (Dionex, Salt Lake City, UT, USA) by a 50/50 *v*/*v* mixture of acetone and hexane at 100 °C with 3 cycles per sample, a 60 % flush volume, a static time of 5 min and purge time of 120 s. The extract was reduced to 10 mL with a nitrogen stream at room temperature, fractionated to 1/10 for soil and to 1/30 for Curlone and Kepone-VIMS, concentrated with a nitrogen stream at room temperature and made up to 1 mL with cyclohexane for analysis. *trans*-Nonachlor was used as a surrogate to correct the results for extraction efficiency, and ^{13}C-CLD was added as an internal standard to mimic as

closely as possible the behaviour of CLD and suppress possible side effects during its analysis.

Extracts were analysed with GC–MS/MS using a GC 450 gas chromatography apparatus provided by BRUCKER (Marne la Vallée, France) equipped with an 1177 injector, a Combi Pal (CTC) autosampler and a 300MS triple quadrupole mass spectrometer (Bruker, Marne la Vallée, France). The injector (operated in splitless mode at 280 °C and 1 mL/min in constant) was equipped with a 4×6.3×78.5-mm liner with fibreglass and Sky™ deactivation (Restek, Lisses, France). The compounds were separated on an Rxi-1MS (30 m, 0.25-mm ID, 0.25 μm) column from Restek (Lisses, France). The column was heated to 50 °C for 1.1 min then to 250 °C with a gradient of 30 °C/min and finally to 310 °C at 10 °C/min and isothermally for 1.5 min. The transfer line was at 310 °C. The ionization source, using electron ionization at 70 eV to produce positive ions, was at 250 °C. The collision gas pressure (argon in CID) was 1.5 mTorr.

LOQs are the following (expressed per kg dw for the soils and per kg humid raw material for the commercial formulations): CLD in soil, 0.03 mg/kg; CLD in Curlone®, 4.5 mg/kg; CLD in Kepone®, 45 mg/kg and 5b-hydroCLD in soil, 0.05 mg/kg; 5b-hydroCLD in Curlone®, 7.5 mg/kg; 5b-hydroCLD in Kepone®, 75 mg/kg.

For the commercial formulations, all analyses were performed in triplicate (three samples for each Curlone® bags and Kepone-VIMS).

Statistical analyses

Relative differences between CLD and 5b-hydroCLD concentrations were investigated by computing 5b-hydroCLD/CLD mass ratios. Statistical properties (using standard tools, see details below) of 5b-hydroCLD/CLD mass ratios were later used to compare relative differences between CLD and 5b-hydroCLD concentrations in commercial formulations and in soils.

Statistical analysis of CLD and 5b-hydroCLD concentrations in commercial formulations

A Kruskal–Wallis rank sum test was used to compare means across sources (Curlone-UAG, Curlone-Cirad, Curlone-IRD, and Kepone-VIMS) and a Bartlett test was used to compare variances. A Shapiro–Wilk test was used to check for lognormality of 5b-hydroCLD/CLD mass ratios. Properties of lognormal distributions were later used to build 95 % confidence intervals (CIs) on 5b-hydroCLD/CLD mass ratios in commercial formulations ($\exp(\mu\pm2\sigma)$ where μ and σ are, respectively, the mean and the standard deviation of log-transformed mass ratios in commercial formulations). Statistical computations were carried out in R (R Core Team 2014).

Statistical analysis of CLD and 5b-hydroCLD concentrations in soils

CLD concentrations in soil samples with quantified 5b-hydroCLD were compared to values in soil samples with unquantified 5b-hydroCLD by using a Welch test (in order to compare means with unequal variances). The Shapiro–Wilk test was used to check for lognormality of 5b-hydroCLD/CLD mass ratios, and properties of lognormal distributions were used to build 95 % CIs on 5b-hydroCLD/CLD mass ratios in soils ($\exp(\mu\pm2\sigma)$, similar to the "Statistical analysis of CLD and 5b-hydroCLD concentrations in commercial formulations" section). Soil samples, which log-transformed 5b-hydroCLD/CLD mass ratio deviated from the mean (μ) beyond three times the standard deviation (σ), were discarded as outliers. Properties of lognormal distributions show that more than 99.7 % of values lie within the interval $\exp(\mu\pm3\sigma)$ and that consequently, the probability to discard a non-outlier sample is less than 0.3 %. Statistical computations were also carried out in R. The present statistical analysis processes soil samples for which CLD and 5b-hydroCLD are both quantified. Soil samples with quantified CLD and unquantified 5b-hydroCLD contain, however, weak but not null information on 5b-hydroCLD/CLD mass ratio. The reason for this is that [5b-hydroCLD]<LOQ implies [5b-hydroCLD]/[CLD]< LOQ/[CLD], that is to say that the 5b-hydroCLD/CLD mass ratio is lower than an upper limit informed by the CLD concentration. The handling of such data—which were discarded so far—requires a more advanced statistical processing which is presented in the next section.

Data censoring

The 5b-hydroCLD and CLD concentrations in soils were subjected to two kinds of data censoring. Data censoring arises when measurements of numerical quantities are partially known. First, the concentrations of 5b-hydroCLD and CLD whose measurement fell below its LOQ were truncated. The numerical value of the measurement was not available, but its range was known to fall between zero and the LOQ, known as left censoring. Second, some concentrations of 5b-hydroCLD were rounded to the nearest 0.01 mg/kg .The numerical value of the measurement was not available, but its range was known to fall within the measured value ±0.005 mg/kg within an interval of amplitude 0.01 mg/kg, known as interval censoring.

The consequences of rounding on 5b-hydroCLD/CLD mass ratios are expected not to be negligible given the low values of 5b-hydroCLD concentrations for some soil samples. As an illustration, rounding to the closest 0.01 mg/kg, a 5b-hydroCLD concentration of

0.015 mg/kg could end to be recorded as a value of either 0.01 or 0.02 mg/kg leading to two possible values of the 5b-hydroCLD/CLD mass ratio that vary by a factor of 2. Left censoring is expected to have dramatic consequences on 5b-hydroCLD/CLD mass ratios for similar reasons.

The analysis which was presented in the "Statistical analysis of CLD and 5b-hydroCLD concentrations in soils" section discarded left-censored samples and could consequently lead to a biased description of 5b-hydroCLD/CLD mass ratios. Moreover, errors due to rounding, as well as errors related to the measurement and sampling processes, and their consequences on 5b-hydroCLD/CLD mass ratios were not accounted for. Hierarchical Bayesian models (HBMs) make relatively easy the handling of random error and censoring processes (Lunn et al. 2012). Authors revisited the analysis of CLD and 5b-hydroCLD concentration data under the form of an HBM, which is presented below. The following analysis handles data originating from soil samples which had quantified CLD and quantified 5b-hydroCLD—as was done previously—completed by soil samples which had quantified CLD and unquantified 5b-hydroCLD.

Statistical modelling of CLD and 5b-hydroCLD concentrations in soils

Measured and latent variables

HBMs make a clear distinction between measured (also called observed) and unmeasured variables (also called unobserved variables, latent variables, and parameters). The numerical run of an HBM leads to the computation of the values (called estimates) of the latent variables which reproduce the observations. Estimates will come with uncertainties which originate from errors in the observations—which are modelled in the HBM as random processes. As an illustration, recorded CLD and 5b-hydroCLD concentrations are measured quantities. Such quantities are some measured versions of unknown, true values of CLD and 5b-hydroCLD concentrations which are altered by errors in the measurement and sampling processes (left censoring, rounding and random errors; see the "Data censoring" section). True values of CLD and 5b-hydroCLD concentrations are not directly measurable and are therefore latent quantities. The measurements of CLD and 5b-hydroCLD concentrations together with the modelling of measurement errors by the HBM will lead to estimated values for latent CLD and 5b-hydroCLD concentrations. The 5b-hydroCLD/CLD mass ratios are as well a latent quantity which will be estimated.

Random measurement errors

Let n be the total number of soil samples and $i \in \{1,\ldots,n\}$ be an index over samples. Let CLD_i^{meas} and $5B_i^{meas}$ be the measured concentrations of CLD and 5b-hydroCLD in soil sample i and CLD_i^{lat} and $5B_i^{lat}$ be their respective latent values. Measured concentrations are modelled as

$$\begin{cases} CLD_i^{meas} \sim Lognormal\left(CLD_i^{lat}\right), \sigma_{CLD}^2\Big), \\ 5B_i^{meas} \sim Lognormal\left(\log\left(5B_i^{lat}\right), \sigma_{5B}^2\right) \end{cases} \quad (1)$$

where $\sigma^2{}_{CLD}$ and $\sigma^2{}_{5B}$ are the variances of the random errors related to the measurement process. In Eq. 1 and in the following ones, parameters for lognormal distributions are the mean and the variance of the variable's natural logarithm, with log the natural logarithm. Lognormal errors model multiplicative errors. Indeed, Eq. 1 is equivalent to $CLD_i^{meas} = CLD_i^{lat} \exp(\delta_i^{meas})$ and $5B_i^{meas} = 5B_i^{lat} \exp(\varepsilon_i^{meas})$ where δ_i^{meas} and ε_i^{meas} are normally distributed errors of mean 0 and variances $\sigma^2{}_{CLD}$ and $\sigma^2{}_{5B}$.

Data censoring

The left-censoring process is modelled by constraining latent values of left-censored concentrations below their respective upper limit. Let $I^T{}_{CLD}$ and $I^T{}_{5B}$ be two subsets of $\{1,\ldots,n\}$ of indexes of soil samples with left-censored CLD and 5b-hydroCLD concentrations. Left censoring is achieved by activating the constraints

$$\begin{cases} 0 \le CLD_i^{lat} \le T_{CLD} & \left(i \in I_{CLD}^T\right), \\ 0 \le 5B_i^{lat} \le T_{5B} & \left(i \in I_{5B}^T\right) \end{cases} \quad (2)$$

where T_{CLD} and T_{5B} are the CLD and 5b-hydroCLD LOQ (see the "Chemical analysis of soils and commercial formulations" section for numerical values for LOQs). The rounding process is modelled in a similar fashion. Let R_{CLD} and R_{5B} be two subsets of indexes of soil samples with rounded concentrations. Rounding is achieved by activating the constraints

$$\begin{cases} CLD_i^{meas} - R_{CLD}/2 \le CLD_i^{lat} \le CLD_i^{meas} + R_{CLD}/2 & \left(i \in I_{CLD}^R\right), \\ 5B_i^{meas} - R_{5B}/2 \le 5B_i^{lat} \le 5B_i^{meas} + R_{5B}/2 & \left(i \in I_{5B}^R\right) \end{cases} \quad (3)$$

where $R_{CLD} = R_{5B} = 0.01$ mg/kg soil dw are the CLD and 5b-hydroCLD rounding precision values. Since consequences of rounding are expected to be prominent for low concentrations, concentrations greater than 0.1 mg/kg soil dw were processed as unrounded.

5b-HydroCLD/CLD mass ratio

Latent CLD and 5b-hydroCLD concentrations are connected to each other through the 5b-hydroCLD/CLD mass ratio

$$r_i = 5B_i^{lat} / CLD_i^{lat}$$

where r_i is the 5b-hydroCLD/CLD mass ratio for soil sample i. The 5b-hydroCLD/CLD mass ratios for all soil samples share similarities which are modelled as

$$r_i \sim \text{lognormal}\left(\log(r), \sigma_r^2\right)$$

where $\log(r)$ and σ_r^2 are the mean and the variance of log-transformed 5b-hydroCLD/CLD mass ratios in soils.

Computations

The HBM was implemented in BUGS language with OpenBUGS version 3.2.1 (Lunn et al. 2012). Implementation details as well as BUGS code are provided in Appendix A.

Results

Commercial formulations

Besides CLD, some 22 compounds could be detected by GC–MS in the commercial formulations including 5b-hydroCLD and traces of Mirex. Their content in CLD and 5b-hydroCLD is presented in Table 1. More information about their chemical composition will be published elsewhere later. 5b-HydroCLD/CLD mass ratios for the four different sources of commercial formulations (Curlone-CIRAD, Curlone-IRD, Curlone-UAG and Kepone-VIMS) are illustrated in Fig. 1. Mean values of the CLD-5b-hydro/CLD mass ratio are identical across sources (Kruskal–Wallis, p=0.44) although with distinct variances (Bartlett, p=0.0095). Taken altogether, 5b-hydroCLD/CLD mass ratios are lognormally distributed (Shapiro–Wilk test on log-transformed mass ratios, p=0.14) with a 95 % CI of 0.55–1.09‰ and a geometrical mean of 0.77‰. This 95 % CI is illustrated in Fig. 2 (blue area).

CLD and 5b-hydroCLD concentrations in soil samples

Among the 810 collected soils, the detection and quantification of CLD and 5b-hydroCLD were as follows: 37.9 % (307 samples) contained both compounds, 36.17 % (293 samples) only CLD, 0.12 % (one sample) only 5b-hydroCLD and 25.8 % (209 samples) no CLD or 5b-hydroCLD. The sample with 5b-hydroCLD only was discarded for the statistical treatment and attributed to analytical error. The concentration of CLD in the 600 samples in which it was detected ranged from 0.01 to 17.4 mg/kg dw (Fig. 2). For each of these CLD concentrations and from the average 5b-hydroCLD/CLD ratio found in the commercial formulations (0.77 ‰, see the "Commercial formulations" section), it was possible to calculate the concentration of 5b-hydroCLD that would be carried to the soil as a CLD accompanying impurity. It resulted from these calculations that 5b-hydroCLD concentrations would be equal or higher than the LOQ in only 1 % of the cases ($5b^{meas}$ >0.01 mg/kg soil dw if CLD^{meas} >0.01/0.77‰=14.08 mg/kg soil dw). In fact, 5b-hydroCLD was quantified in 51.2 % of the soil samples containing CLD. It is worth noting that the CLD concentrations (0.10 to 17.4 mg/kg, red symbols in Fig. 2) of the samples containing both CLD and 5b-hydroCLD were significantly (Welch test on log-transformed CLD concentrations, $p<10^{-16}$) higher, on average 10.2 times, than the CLD concentrations (0.01 to 3.17 mg/kg; green symbols, Fig. 2) of the samples where 5b-hydroCLD could not be quantified.

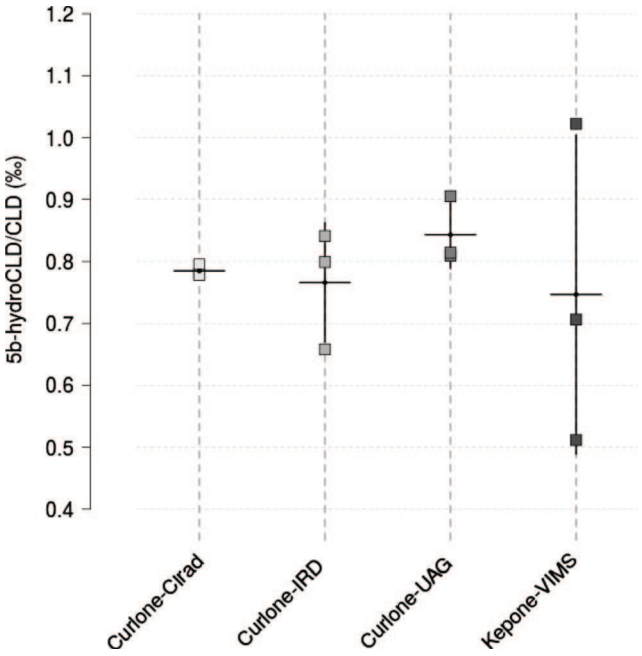

Fig. 1 5b-HydroCLD/CLD mass ratios (replicate values, *squares*; means (n=3), *horizontal lines*; means±standard error, *vertical lines*) for four commercial formulations (Curlone-Cirad, Curlone-IRD, Curlone-UAG and Kepone-VIMS) processed by accelerated solvent extraction (ASE)

Statistical analysis of 5b-hydroCLD/CLD mass ratio in soils

The 5b-hydroCLD/CLD mass ratios for the 307 samples where CLD and 5b-hydroCLD were both quantified ranged between 1.7 and 1000‰, with 95 % of the values in the 4–100 ‰ range, six values were between 100 and 300‰, and two values were equal to 1000‰. The latter two soil samples were discarded (the "Statistical analysis of CLD and 5b-hydroCLD

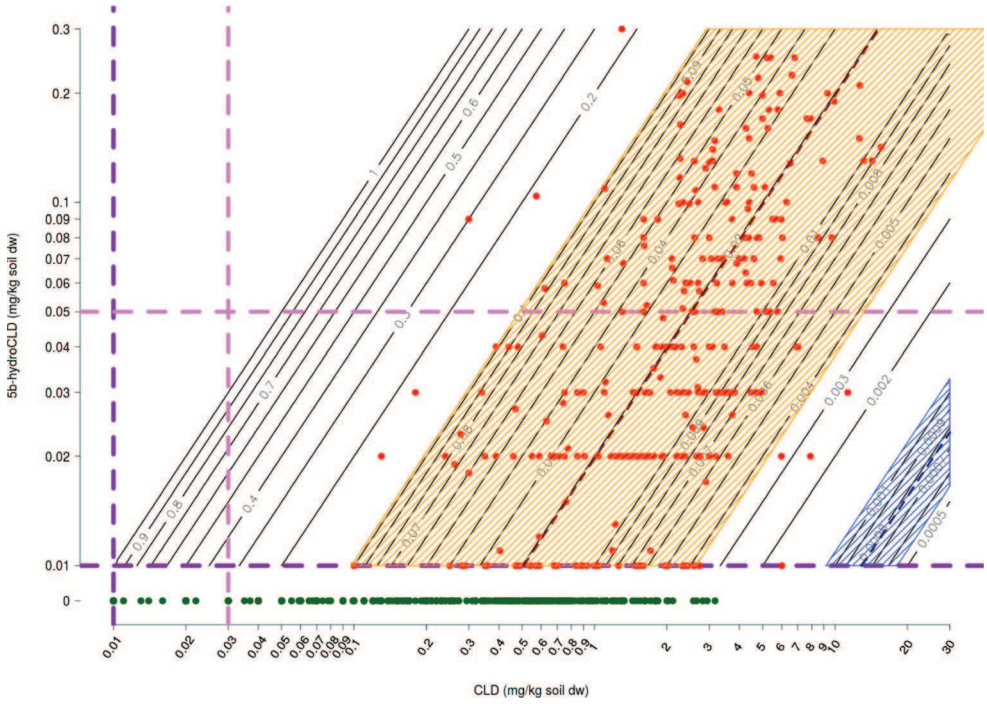

Fig. 2 CLD and 5b-hydroCLD concentrations (quantified 5b-hydroCLD, *red circles*; non-quantified 5b-hydroCLD, *green circles*) in soils sampled in Martinique between 2007 and 2012. The 95 % CI range of 5b-hydroCLD/CLD mass ratios in commercial formulations corresponds to the *hatched blue area* and the average to the *dashed blue line*. The 95 % CI range of 5b-hydroCLD/CLD mass ratio in soils with quantified 5b-hydroCLD corresponds to the *hatched orange area* and the average to the *dashed red line*. Lines of constant 5b-hydroCLD/CLD mass ratio are represented as *oblique black lines*. LOQs for CLD and 5b-hydroCLD are plotted as *horizontal and vertical dashed lines* (DAAF, *violet*; BRGM, *pink*)

concentrations in soils" section). The 5b-hydroCLD/CLD mass ratios of the remaining 305 samples were lognormally distributed (Shapiro–Wilk test on log-transformed ratios, p=0.56). The geometric mean ratio was 19.7‰ with 95 % of the values in the range 4.1–99.2‰. In other words, CLD concentration in soils was on average 50 times higher than 5b-hydroCLD concentrations, and the 5b-hydroCLD/CLD mass ratio in soils was on average 25 times higher than the ratio in commercial formulations.

Lines of constant mass ratio $5B^{meas}/CLD^{meas}=r$, with r ranging from 0.5 to 1000‰, are illustrated in Fig. 2. Given that $\log(5B^{meas})=\log(CLD^{meas})+\log(r)$, such lines are, in a log–log plot, straight lines of slope 1 and intercept the value of the mass ratio. The estimated mean mass ratios in soils together with the 95 % CI of mass ratios are represented in Fig. 2 (orange area). Rounding off 5b-hydroCLD concentrations to the nearest 0.01 mg/kg soil dw is plainly visible as horizontal patterns in the scatter plot of Fig. 2.

Statistical modelling of 5b-hydroCLD/CLD mass ratio in soils

The analysis of extraction yield data for the soils shows that CLD and 5b-hydroCLD extraction yields were lognormally distributed (Shapiro–Wilk test on log-transformed extraction yields; CLD, p=0.13; 5b-hydroCLD, p=0.21). Estimated standard deviations for log-transformed yields were used to model random errors on CLD and 5b-hydroCLD concentrations in the HBM ("Random measurement errors" section; σ_{CLD}=0.22 and σ_{5B}=0.16). A detailed count of soil samples for which CLD and/or 5b-hydroCLD concentrations were left-censored, rounded, or uncensored is provided in Table 2. The 598 soil samples with quantified CLD—with (305) or

Table 2 Soil samples from DAAF/BRGM in which CLD (rows) and 5b-hydroCLD (columns) concentrations were below the LOQ, above the LOQ and rounded to the nearest 0.01 mg/kg soil dw, and above the LOQ and not rounded (uncensored)

		5b-HydroCLD			
		<LOQ	Rounded	Uncensored	Total
CLD	<LOQ	207/2[b]	1/0[a]	0/0	208/2
	Rounded	66/1[d]	2/0[a]	0/0	68/1
	Uncensored	160/66[d]	202/0[c]	99/4[c]	461/70
	Total	433/69	205/0	99/4	737/73

[a] Three soil samples were discarded as outliers

[b] Samples with both CLD and 5b-hydroCLD concentrations below the LOQ were discarded for further analysis

[c] Samples used in the statistical analysis (the "Statistical analysis of CLD and 5b-hydroCLD concentrations in soils" section)

[d] Additional samples used in the modelling analysis ("Statistical modelling of CLD and 5b-hydroCLD concentrations in soils" section)

without (293) quantified 5b-hydroCLD—were processed by the HBM. The geometric mean of the 5b-hydroCLD/CLD mass ratio is estimated to r=15.0‰ (95 % CI 13.7–16.4‰). The latter CI illustrates the degree of confidence that can be placed on the estimate of the mean ratio. As it will be discussed in the "Caution about CLD half-life calculation" section, the mean 5b-hydroCLD/CLD mass ratio which was estimated in the "Statistical analysis of 5b-hydroCLD/CLD mass ratio in soils" section (19.7‰) is biased with respect to what is found by processing all available data. The 95 % range of 5b-hydroCLD/CLD mass ratios in soils is obtained by using Eq. 5, $\exp(\log(r)\pm 2\sigma_r)$. Standard deviation σ_r is estimated to 0.84 (95 % CI 0.77–0.92). Consequently, 95 % of the 5b-hydroCLD/CLD mass ratios lie in 2.8–80.7‰. The HBM also provides point and 95 % interval estimates of latent CLD and 5b-hydroCLD concentrations, which are illustrated in Fig. S1 (Supplementary Material), and of the 5b-hydroCLD/CLD mass ratio (Fig. S2, Supplementary Material). The Bayesian approach narrowed the range and lowered the mean of the 5b-hydroCLD/CLD mass ratio in soils with respect to what was found in the "Statistical analysis of 5b-hydroCLD/CLD mass ratio in soils" section. The estimated soil 5b-hydroCLD/CLD mass ratio remains, however, significantly greater than what was found in commercial formulations.

Discussion

Results clearly indicate that 5b-hydroCLD/CLD mass ratios in Martinique soils are significantly greater than those in commercial CLD formulations. The authors hypothesize that this is due to CLD transformation into 5b-hydroCLD in soils. A series of elements running counter to this hypothesis are discussed in the "Why soil 5b-hydroCLD cannot only be attributed to the impurities present in Curlone® and Kepone®" section. Potential formation of 5b-hydroCLD by CLD dechlorination is discussed in the "Potential formation of 5b-hydroCLD by CLD dechlorination" section. The interest of the advanced processing of data with a Bayesian approach and perspectives are presented in the "Caution about CLD half-life calculation" section.

Why soil 5b-hydroCLD cannot only be attributed to the impurities present in Curlone® and Kepone®

Non-representativeness of the data on formulations

The representativeness of the 5b-hydroCLD/CLD mass ratios obtained for the commercial formulations can be questioned since only four different sources were analysed and that, moreover, two of them (Curlone-UAG and Curlone-IRD) were formulated on the same date (September 1983) although they corresponded to independent Curlone® bags sampled in different geographical locations, Guadeloupe and Martinique, respectively, (Table 1). The two other samples brought, however, more diversity, particularly the Kepone-VIMS that corresponded to technical-grade CLD (active ingredient of Kepone® 5 %) manufactured in the USA before 1976, whereas the three Curlone® samples were necessarily formulated with technical-grade CLD produced in Brazil after 1982. As such, the four samples can be considered to be sufficiently representative of the diversity of the commercial formulations applied in FWI between 1972 and 1993. It is therefore noticeable that the 5b-hydroCLD/CLD ratios found in this study for the Kepone-VIMS and the three Curlone® sources were not statistically significantly different (Fig. 1 and the "Commercial formulations" section). This is consistent with the fact that the chemical processes used to produce technical-grade CLD in the USA and Brazil were apparently the same according to a French parliamentary report (Beaugendre et al. 2005). A thorough review of the patent literature does not indicate also the development of any new process for the manufacture of CLD after 1976 (last patent available by Moore and Hundtofte 1976 assigned to Allied Chemical Corporation). All this is indicative that the higher ratios observed in the soils cannot result from the spreading of commercial formulations that would have significantly higher 5b-hydroCLD/CLD ratios than those found in the present study. The last but not least point which strengthens this conclusion is that the highest 5b-hydroCLD/CLD ratio (1‰) obtained for the Kepone® formulation remains 20 times lower than the mean ratio observed in soils (this security margin is even greater when considering the Curlone® formulations). One may therefore consider the data on 5b-hydroCLD/CLD ratios in formulations to be robust.

Different physical behaviour of 5b-hydroCLD and CLD resulting in different persistence in soil

In the absence of biotic or abiotic degradability, the main factors that may influence the 5b-hydroCLD/CLD ratios in soils, after the spreading of the commercial formulations, would be a differential behaviour of 5b-hydroCLD and CLD in terms of volatilization, mobilization by water (leaching or loss with run-off water under the action of rain) and capacity to remain adsorbed on soil particles.

The volatility and solubility of 5b-hydroCLD have never been determined experimentally. From thermodynamic data, Dolfing et al. (2012) have estimated that 5b-hydroCLD has a Henry's constant of 0.00284 Pa m^3/mol, which is very close to the value of 0.0025 Pa m^3/mol reported for CLD in the literature that classifies it as a very poorly volatile compound (Faroon et al. 1995). The same team has also estimated by other means that 5b-hydroCLD would be five times more soluble than CLD. This increased solubility is in agreement with the fact that 5b-hydroCLD elutes before CLD during gas

or liquid chromatographic analysis using apolar columns (Carver and Griffith 1979; George et al. 1986; Belghit et al. 2015; this article, data not shown). This elution order is indeed experimental evidence that 5b-hydroCLD is more polar than CLD and so necessarily more soluble in a polar solvent like water. In the same way, if 5b-hydroCLD is more water soluble that CLD, then it also has necessarily a lower *Kow* (octanol water partition coefficient) since *Kow* and solubility are inversely correlated (*Kow* is a measure of the hydrophobicity of a compound). Remembering that 5b-hydroCLD has one Cl less than CLD, the previous deduction is fully supported by the literature where it is now established that the *Kow* of haloorganic compounds decreases concurrently with the decrease of the number of halogen atoms bound to the carbon skeleton (Kuramochi et al. 2004a; van Noort 2009; Gewurtz et al. 2009; Bettina et al. 2011). The propensity of a non-ionic organic compound to partition between an aqueous solution and soil is commonly described by the soil water distribution coefficient normalized to the soil organic content, *Koc*. This coefficient is well known to be positively correlated with *Kow*, which means that compounds having higher or lower *Kow* will also have higher or lower *Koc* (Nguyen et al. 2005). According to the above discussion, it appears that if 5b-hydroCLD has a lower *Kow* than CLD, it will also have a lower *Koc*.

Although no experimental data exist about the physical properties of 5b-hydroCLD, the previous considerations show that it should have a Henry's constant similar to CLD but a higher solubility and lowers *Kow* and *Koc* (Kuramochi et al. 2004b). This indicates, on one hand, that 5b-hydroCLD and chlordecone must have comparable and extremely low volatilization potential (if any) from soils and, on the other hand, that 5b-hydroCLD should be more prone than CLD to desorption and so comparatively to an increased transfer from soil to water and plants. Such an increased transfer capacity is in line with the high 5b-hydroCLD/CLD ratios (5–232‰, average±SD=63±62) that have been found in 58 samples of groundwater of Martinique collected at the occasion of governmental surveys (period 2010 to 2012) performed to monitor their quality (BRGM, unpublished results).

In the absence of any abiotic or biotic transformation of CLD, such an increased transfer would result over time in a quicker decrease of 5b-hydroCLD concentration in soil than CLD, and so, over the two decades separating the last Curlone® application and the sampling of the soils analyzed during this study, one could expect a decrease of the 5b-hydroCLD/CLD ratio in soil rather than the significant increase that is observed. This clearly shows that such evolution cannot be attributed to the physical properties of 5b-hydroCLD.

5b-hydroCLD from another source than the CLD applied to the soils

So far, compounds of the bishomocubane family to which 5b-hydroCLD and CLD belong are not known to be naturally synthesized in the earth (Phillip Eaton, "father of cubane", personal communication). Any 5b-hydroCLD detected in the environment must then necessarily come from a man-made bishomocubane structure. It is known that 5b-hydroCLD may be formed by photoreaction with sunlight of the perchlorinated bishomocubane pesticides, Mirex ($C_{10}Cl_{12}$) and CLD (Ivie et al. 1974) and so also from a compound such as Kelevan that is a source of CLD upon breakdown of the bond connecting its CLD and levulinate moieties (Maier-Bode 1976). However, there is no evidence that Kelevan has ever been used in the FWI. Some Mirex was applied legally in Guadeloupe between 1968 and 1978 for control of the cassava ant (*Acromyrmex octospinosus*), but the amount used was rather small (58.6-kg active ingredient, Bellec and Godard 2002) compared to 300 t of CLD. Such a use of Mirex was, however, non-existent in Martinique that was never colonized by this ant (Patrick Quénéhervé, IRD-CAEC nematology laboratory, Martinique, personal communication). In these conditions, Mirex is not routinely searched for in environmental matrices from Martinique. A monitoring campaign performed in 2002 has shown, nevertheless, that Mirex could be detected in 69 % of the 75 soils sampled at this occasion at an average concentration of 0.02 mg/kg soil dw (Bellec and Godard 2002). As indicated in the "Commercial formulations" section, Mirex is also present as an impurity in the Curlone® and Kepone® commercial formulations that were once spread in FWI. Taking into account as follows: (1) the amount of these products applied in Martinique (200 t=2/3 of 300 t since 2/3 of FWI banana production is in Martinique), (2) the surface of the island covered by banana plantations between 1972 and 1993 (12,400 ha with 49 % of this surface corresponding to andosol), (3) the soil bulk densities (0.71 and 0.941 kg soil dw/soil m^3 in average for andosol and non-allophonic soils, respectively), (4) the usual tilling depth (30 cm) and (5) the Mirex/CLD ratios in the commercial formulations (minimum 1.41‰, maximum 3.18‰), it can be estimated that the concentration of Mirex resulting from the sole spreading of Curlone® and Kepone® would be of 0.008 to 0.024 mg Mirex/kg soil dw. This means that all the Mirex detected in the soils of Martinique can be attributed to the Curlone® and Kepone® and confirms that no other significant uncontrolled source of Mirex was used on the island.

A 100 % conversion of the Mirex present in the commercial formulations into 5b-hydroCLD (1 mol gives 1 mol) after their spreading would result in an increase of the soil 5b-hydroCLD/CLD ratio from an average value of 0.77‰ (the one of the formulations) to an average value of 2.61‰, which

remains well below the average ratio of 19.7‰ found in these soils.

Such a level of conversion of Mirex into 5b-hydroCLD is anyway completely unrealistic. As an example, in the USA, only 2.2 and 8.5 % of Mirex spreads in a field in 1962, at a concentration of 1 ppm, were recovered 12 years later in the soils of this field under the form of CLD and 5b-hydromirex, respectively (Carlson et al. 1976), which are known precursors of 5b-hydroCLD under the action of light and UV (Alley et al. 1974; Ivie et al. 1974). The production of 5b-hydroCLD from these compounds occurs, however, with an extremely slow kinetics, even when sunlight exposure is optimum (Ivie et al. 1974), which is obviously not the case of a compound buried in soil.

All the previous considerations confirm that the increased 5b-hydroCLD/CLD mass ratio observed in soils may not be attributed to another source of 5b-hydroCLD than the CLD present in the commercial formulations.

Difference in 5b-hydroCLD and CLD extraction yields between the soils and the formulations

Since Martinique soils and CLD formulations are quite different in composition and total CLD content, the possibility exists of differences between the two matrices with respect to 5b-hydroCLD and CLD extraction yields. An extraction yield of 5b-hydroCLD from the soil greater than that from the formulation, or the opposite for CLD, would explain the observed 5b-hydroCLD/CLD ratios in soils being greater than those in the CLD formulations.

To test this possible effect, complementary analyses were conducted on the two available Curlone® formulations with the most contrasted 5b-hydroCLD/CLD ratios and a soil sample representative of each of the three major soil types (andosol, ferralsol and nitisol) included in the database.

Briefly, the standard addition method was applied to the five matrices in sixfold replicates with 100 and 200 % of the previously measured 5b-hydroCLD and CLD concentrations in these formulations and soils. The extraction and analysis procedure was as described in the "Chemical analysis of BRGM soils and CLD commercial formulations" section.

Results (Table 3, Fig. S3 and Appendix B in supplementary information online) show that the 5b-hydroCLD extraction yields do differ significantly neither between soils (a group, see Appendix B) nor between Curlone® samples (d group) but are significantly higher in Curlone® than in soil matrices (a versus d). CLD extraction yields are equal in all matrices (group c). Extraction yields in soil are equal for 5b-hydroCLD and CLD (a group). Extraction yields in Curlone® are higher for 5b-hydroCLD (d group) than for CLD (c group). Yields greater than 100 % are commonly observed when dealing with trace contaminants (see for instance French guideline AFNOR NF T90-210), all the more so here when the standard addition is only one or two times the initial amount. The mean ratio of '5b-hydroCLD extraction yield'/'CLD extraction yield' is 0.89 and 1.24 for soils and Curlone®, respectively. This means that the ratios of 5b-hydroCLD/CLD concentrations measured in the soils should be multiplied by 1.24/0.89=1.39 to be directly comparable to those measured in the formulations.

As a consequence, the real 5b-hydroCLD/CLD concentration ratios in soils should not be on average 25 times but almost 35 times greater than in the formulations. This definitely shows that the different ratios of 5b-hydroCLD/CLD concentrations between the formulations and the soils cannot result from an analytical extraction artefact.

Back-calculation of CLD input based on measured soil 5b-hydroCLD concentration and amount found as an impurity in commercial formulations

On average, 5b-hydroCLD has been detected at a concentration of 0.042 mg/kg soil dw in half of the soils analyzed in this study. Based on the 5b-hydroCLD/CLD ratios found in the commercial formulations (0.5 to 1‰), concentrations of CLD as high as 42 to 84 mg/kg (=0.042/0.5 or 0.042/1‰) should have been found in these soils. In the absence of any loss by transfer or biodegradation, obtaining such CLD concentrations would have implied the spreading of some 960 to 2900 t[5] of CLD over the 12,400 ha of Martinique covered by banana crops between the 1972 and 1993 period. This would represent half, or more than one time and a half, the CLD amount ever manufactured in the world (1800 t, see "Introduction") and so corresponds to unrealistic or impossible amounts. As previously mentioned, it is indeed widely accepted now that no more than 300 t of CLD was used in the FWI (Le Déaut and Procaccia 2009). Again, the simple calculations presented above lead to the conclusion that the amount of 5b-hydroCLD found in the soils of Martinique cannot be attributed to the sole impurities present in the applied Curlone® and Kepone®. At most, these impurities could explain 6 to 18 % of the average 5b-hydroCLD concentrations found in the soils.

Potential formation of 5b-hydroCLD by CLD dechlorination

According to all the arguments presented in the "Why soil 5b-hydroCLD cannot only be attributed to the impurities present in Curlone® and Kepone®" section, it is now clear that the only explanation for the high 5b-hydroCLD/CLD ratios

[5] *=12,400×'soil mass/ha'×[5b-hydroCLD]/'‰ 5b-hydroCLD in commercial formulations' with 'soil mass/ha'='soil bulk density'×'tillage depth'×10000; see the "5b-HydroCLD from another source than the CLD applied to the soils" section for numerical values for soil bulk density and tillage depth and Cabidoche et al. (2009)

Table 3 Recovery yields (means ±std. dev.) of CLD and 5b-hydroCLD after standard additions (n=6; two levels in triplicate) to the three main Martinique soil types and two Curlone® formulations formerly applied on these soils

Matrix	CLD extraction yield (%)	5b-HydroCLD extraction yield (%)	Ratio of 5b-hydroCLD and CLD extraction yields
Andosol	89±7	85±12	0.96
Nitisol	93±6	82±9	0.88
Ferralsol	91±6	76±8	0.83
Curlone-UAG	97±12	133±12	1.37
Curlone-IRD	118±34	131±20	1.11

observed in the soils of Martinique is that CLD has been less inert than initially thought and that a dechlorination of CLD occurred in these soils. The biotic or abiotic nature of such dechlorination is difficult to establish, a priori, but several hypotheses may be drawn according to the data available in the literature about this compound and other chlorinated products (Fig. 3).

For four decades now, it has been established for instance that 5b-hydroCLD can be formed from CLD by photoreaction with UV light (Alley et al. 1974) and most probably also under the action of sunlight (Ivie et al. 1974). Such a photoreaction would, of course, be restricted to the soil surface. Nevertheless, part of the CLD stock, present in the first 30 cm of the soil, could be regularly exposed to sunlight from tilling the soil from time to time. Taking into account the fact that also 40 years has elapsed since CLD was used for the first time in the FWI, and that CLD spread was abandoned 20 years ago, such an action of sunlight may not be as insignificant, particularly, when considering that the latitude of this geographical area results in very high sun exposure.

The possibility of a microbial dechlorination of CLD cannot also be discarded. As mentioned in the "Introduction", such dechlorination should occur preferentially under anaerobic conditions, while the FWI soils are macroscopically oxic. Nevertheless, the work of Orndorff and Colwell, published back in 1980, provided convincing evidence that a strict aerobe, such as *Pseudomonas aeruginosa*, a common soil bacterium, was able to dechlorinate CLD into 5b-hydroCLD. However, it was found that this bacterium could not use it as a sole carbon and energy source and needed the presence of another carbon source in the surrounding environment. In any case, it is well established that anoxic microniches form readily inside the aggregates of well-aerated soils (e.g. Sexstone et al. 1985) where CLD dechlorination processes such as those described by Schrauzer and Katz (1978) using vitamin B_{12} and including the formation of 5b-hydroCLD may well be performed by anaerobic dehalogenating bacteria (Fig. 3). It is indeed recognized now that a cobalamin is involved in the catalytic activity of the dehalogenases of aforesaid bacteria and that they are vitamin B_{12} dependent (Smidt and de Vos 2004).

Finally, the potential role of the iron forms present in the FWI soils may have been overlooked. Belghit et al. (2015) have clearly shown that Fe° can be used as an electron donor for CLD dechlorination and that 5b-hydroCLD is one of the two monohydroCLDs that are transitionally formed during the process. Fe° obviously does not exist as such in FWI volcanic soils, but these types of soils are known to contain iron oxide forms such as $Fe(OH)_3$ (ferrihydrite), α-Fe_2O_3 (hematite) and α-FeOOH (goethite) (e.g. Parfitt et al. 1988; Maejima et al. 2000; Schaefer et al. 2008). In soil anoxic microniches, it is now realized that these iron oxides form a FeIII/FeII iron cycle under the action of iron-reducing bacteria and that the 'biogenic' FeII that is formed during the FeIII reduction is an excellent electron donor. The iron oxides/FeII couples have low redox potentials (see redox scale of Fig. 3), although not as low as Fe°/FeII. The coupling of this FeIII/FeII cycling to the dechlorination of chlorinated compounds has been demonstrated at lab scale (Li et al. 2008, 2009) and could work for the CLD/5b-hydroCLD redox couple. CLD/5b-hydroCLD has indeed a redox potential of +414 mV (Dolfing et al. 2012), which indicates that it can act as an electron acceptor for the 'iron oxide'/FeII couples, this part of the process being merely abiotic (Fig. 3).

The different hypotheses that can be drawn for 5b-hydroCLD formation from CLD are summarized in Fig. 3. It is impossible to estimate if they all work together or the importance of one over the others. Anyway, one must also keep in mind that there is no reason why CLD dechlorination should not proceed further and 5b-hydroCLD should not be an end product. The actual levels of 5b-hydroCLD in the FWI soils that represent only 19.7‰ of the CLD still present in the soil suggest very slow conversion rates of CLD to 5b-hydroCLD. This maybe explains why further dechlorination products have not been detected, so far, in these soils, due to the expected resulting very low concentrations. For instance, contrarily to what occurred with US soils, no traces of dihydroCLD were found in Guadeloupean soils having 5b-hydroCLD/CLD ratios—7.1 to 18.33‰—in the range of those observed in Martinique (Borsetti and Roach 1978; Martin-Laurent et al. 2014). The 5b-hydroCLD may therefore be just the tip of the iceberg. As observed by Belghit et al. (2015) when contacting CLD with Fe° in an aqueous phase, it is possible also that another monohydroCLD isomer among the four that exist may have formed predominantly in the soils and that it was never observed because it was not searched due to the lack of commercial analytical standards. Interestingly,

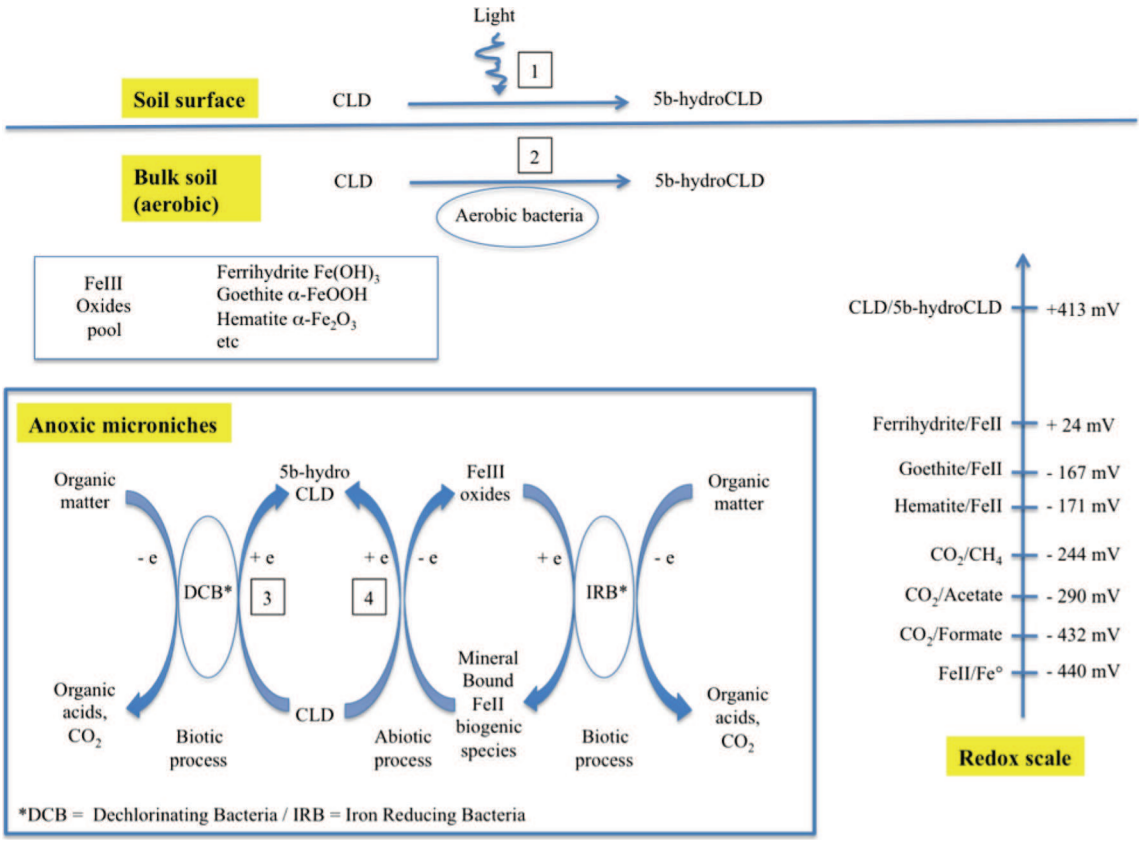

Fig. 3 Hypothetical abiotic and biotic processes that may contribute to the formation of 5b-hydroCLD through CLD dechlorination in the different soil compartments (surface, bulk soil, anoxic microniches): photoreaction (*1*), direct microbial dechlorination by aerobic (*2*) and/or anaerobic (*3*) microorganisms and indirect abiotic dechlorination through the FeIII/FeII cycle mediated by iron reducing bacteria (*4*). The CLD/5b-hydroCLD redox potential value given in the redox scale corresponds to that calculated by Dolfing et al. (2012). All the other redox potentials were taken from Majzlan (2013) except for FeII/Fe° (Dolfing et al. 2008). All redox potentials were calculated for a pH of 7 and standard conditions except for the iron oxides—see Majzlan (2013) for further details

the second monohydroCLD isomer that formed during the Belghit et al. (2015) experiments was detected in the water of a natural pond close to banana fields in Martinique (BRGM, unpublished data). All this broadens the perspectives for searching for solutions employing remediation.

Caution about CLD half-life calculation

It is tempting to compute the CLD half-life in soils from the mean 5b-hydroCLD/CLD mass ratios that the authors have reported. The authors warn against this operation since the computation of the half-life would ground upon several assumptions that are clearly transgressed. It is, however, interesting to move forward in this computation, which points out knowledge gaps and pitfalls. Namely, under the assumptions of (1) a first-order dechlorination process with a constant rate over (2) time and (3) space, (4) without any other transformation pathway of CLD and (5) without further transformation of 5b-hydroCLD, without any (6) lixiviation or (7) run-off transfer of CLD or 5b-hydroCLD in soils, with (8) a known quantity of commercial CLD formulation in which (9) 5b-hydroCLD/CLD mass ratio is known, are applied at a (10) single, (11) known time. All of the above-mentioned 11 assumptions, however, would need to be validated. To the authors' point of view, it is not reasonable to compute dechlorination rate and CLD half-life from their data and above formulas in view of the unrealistic assumptions that would be required to do so. The authors think, however, that computing dechlorination rate and CLD half-life is an appealing perspective. The next steps towards this goal would be (1) the careful investigation of the consequences of the lack of validity of the assumptions on the estimates of the dechlorination rate and CLD half-life and (2) the designs of a more advanced experimental survey and model that would allow to relax some of these assumptions.

Statistical computing and further analysis

As explained in the "Statistical analysis of CLD and 5b-hydroCLD concentrations in soils" section, soil samples with quantified CLD and unquantified 5b-hydroCLD contain weak but not null information on the 5b-hydroCLD/CLD mass

ratio. The most advisable computation of the statistical properties of the 5b-hydroCLD/CLD mass ratios in soils should therefore include such samples. It is not trivial to account for data censoring using standard statistical tools. As the authors have shown, it is relatively easy using HBM. In this case study, however, information on the 5b-hydroCLD/CLD mass ratio which is contained in the 305 soil samples with both quantified CLD and 5b-hydroCLD surpasses information which is contained in the 293 soil samples with only quantified CLD. Consequently, the estimate of the mean 5b-hydroCLD/CLD mass ratio is similar using the 293 samples or all. Results have shown, however, that the result from the first analysis using an incomplete dataset (19.7‰) is biased with respect to the results of the second one using the full dataset (95 % CI 13.7–16.4 ‰). The interest to include rather than discard censored data is expected to increase on case studies with smaller amounts of uncensored data.

The authors computed the ratio CIs of the 305 soil samples with both quantified CLD and 5b-hydroCLD (Fig. S2). Ratio uncertainties could be considered in a further analysis by using weighted least squares when interconnecting ratios to covariates (see later below). The authors also managed to compute ratio CIs for the 293 soil samples with unquantified 5b-hydroCLD (Fig. S2). Such CIs illustrate the low—but not null—level of information that is contained in such soil samples; CI of samples with null information should be equal to the reported range 2.8—80.7‰. The authors also managed to compute the likely range of values of respective latent 5b-hydroCLD concentrations. For that purpose, the HBM basically finds the values for $5b^{lat}$ when $5b^{meas}$ <LOQ such that the ratio in the soil sample is lower than LOQ/CLD^{meas} and within the range of ratios that are indicated by the remaining soil samples. This operation relies on the assumption that values in soil samples follow a distribution of known form, here lognormal ("5b-HydroCLD/CLD mass ratio" section). This choice was strongly supported by our data (Shapiro–Wilk test on log-transformed ratios, p=0.56; the "Statistical analysis of 5b-hydroCLD/CLD mass ratio in soils" section).

The increase of 5b-hydroCLD/CLD mass ratios in soils as a function of time is a manifestation of underlying biotic/abiotic processes that alter CLD. It would be interesting to estimate the parameters (with CIs) that more faithfully describe such processes. Such parameters are interconnected to 5b-hydroCLD and CLD concentrations, as it was illustrated concerning the dechlorination rate while presenting the simple ordinary differential equation (ODE) model in the "Potential formation of 5b-hydroCLD by CLD dechlorination" section. HBM can efficiently handle non-linear equations and ODEs. It has been shown that assumptions which lead to the dechlorination model are unrealistic and would need to be revised. Accounting for such revisions by extending the HBM which was presented in the case study, by including biotic/abiotic processes, is an interesting perspective. Latent variables would be in that case the parameters of the biotic/abiotic processes such as the dechlorination rate. CIs of model parameters would be computed as the authors did with the mean 5b-hydroCLD/CLD mass ratio.

Other further investigations will lead to combine the location of soil samples, and their CLD and 5b-hydroCLD content, in order to investigate cartographically the paedo-climatic (sun, type of soil, rain intensity and slope) and land use (crop alternation, banana plantation frequency and chronology) drivers. If such investigations do not lead to correlate high 5b-hydroCLD/CLD mass ratios with abiotic parameters, the microbial flora and fungi composition of the soils presenting the said characteristic could be analysed like Merlin et al. (2014) and Mercier et al. (2013) prefigured. The consideration of covariates could be achieved with a standard multivariate regression analysis. Another option is to extend the authors' HBM by connecting latent variables (5b-hydroCLD/CLD mass ratio, dechlorination rate, etc.) to paedo-climatic covariates. The interest of the latter approach is the possibility to propagate errors originating from the measurement and sampling processes into uncertainties on multivariate regression parameters.

Conclusion

CLD persistence in the environment impedes us to study its fate in vitro, while the present statistical analysis highlights the unexplained high amount of 5b-hydroCLD in soil associated with the CLD spread. The hypothesis proposed for explaining why 5b-hydroCLD/CLD ratios in soils exceed the corresponding ratio in commercial formulation leads to the inverse demonstration: 5b-hydroCLD should be preferentially eluted from soil by water and may be metabolized, strengthening the significance of the statistical evidence demonstrating that 5b-hydroCLD amounts in field soil cannot be justified by its sole input as an impurity present in the Kepone® and Curlone® commercial formulations. In fact, the 5b-hydroCLD corresponding to the impurity could only justify 1/25 of the 5b-hydroCLD content observed in the field. The bishomocubane structure of the compounds invalidates all the other origins unless CLD. All the investigations dealing with the differential transfer of 5b-hydroCLD compared to CLD lead to promote a decreasing mass ratio in situ compared to the formulation, the opposite of the trend observed. Previously, considered as a by-product due to CLD synthesis, 5b-hydroCLD turns to be a highly probable dechlorination product of CLD. However, the details on 5b-hydroCLD formation are still to be determined although some potential pathways for this formation could be advanced in the paper.

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Dedication In his 73rd year, this article is dedicated to Dr. G. Wayne Sovocool for his contributions to the use of mass spectral tools for the identification of organic pollutants. Among his achievements, he was a member of the US EPA team who 37 years ago made a breakthrough in the GC/MS analysis of chlordecone and of its mono-, di-hydro and chlordecol derivatives (see reference of Harless et al. 1978). Since then, this work remains a source of key information for those who are involved in chlordecone environmental studies. We also thank Wayne for his advice in order to improve the English of the present article.

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Appendix A – Computational details

Posterior distribution samples of latent variables can be efficiently simulated using a Markov Chain Monte Carlo (MCMC) method. The simulation of posterior samples of a HBM, from a description of the statistical properties and of the connections between variables (equations (1)-(4)), was achieved by OpenBUGS. Parameters of interest were provided low informative priors (CLD_i^{lat} Lognormal(0,10000), r Lognormal(0,10000)). Convergence was investigated by the inspection of the values of simulated samples. Once convergence was reached, 10000 posterior samples of the model latent variables were simulated. Point estimates reported in the text and Figures are posterior means and reported 95% confidence interval estimates are 2.5% and 97.5% posterior marginal quantile estimates.

The BUGS code to process 5b-hydroCLD and CLD concentrations in soil by accounting for data censoring (LOQ, rounding) and random measurement errors is provided below. The model processes left-censored data (index `I_CLD_thresholded[i] and I_HYDRO5B_thresholded[i])`, rounded data `(I_CLD_rounded[i] and I_HYDRO5B_rounded[i])`, and remaining uncensored data `(I_CLD_uncensored[i] and I_HYDRO5B_uncensored[i])`. BUGS parameters for lognormal distributions are – contrary to the rest of the paper – the mean and the precision of the variable's logarithm (`pi_conc_CLD, pi_conc_HYDRO5B, and pi_ratio`). Precisions are inverse of their respective variances.

```
model ratio{
      # if uncensored
      for(i in 1:n_CLD_uncensored){
            CLD_mes[I_CLD_uncensored[i]]                                    ~
dlnorm(CLD_log[I_CLD_uncensored[i]],pi_conc_CLD)
            CLD_bis[I_CLD_uncensored[i]] <- CLD_mes[I_CLD_uncensored[i]]
      }
      for(i in 1:n_HYDRO5B_uncensored){
            HYDRO5B_mes[I_HYDRO5B_uncensored[i]]                             ~
dlnorm(HYDRO5B_log[I_HYDRO5B_uncensored[i]],pi_conc_HYDRO5B)
            HYDRO5B_bis[I_HYDRO5B_uncensored[i]]                            <-
HYDRO5B_mes[I_HYDRO5B_uncensored[i]]
      }
      # if left-censored
      for(i in 1:n_CLD_thresholded){
            CLD_bis[I_CLD_thresholded[i]]                                    ~
dlnorm(CLD_log[I_CLD_thresholded[i]],pi_conc_CLD)I(0,threshold_CLD[I_CLD_th
resholded[i]])
      }
      for(i in 1:n_HYDRO5B_thresholded){
            HYDRO5B_bis[I_HYDRO5B_thresholded[i]]                            ~
dlnorm(HYDRO5B_log[I_HYDRO5B_thresholded[i]],pi_conc_HYDRO5B)I(0,threshold_
HYDRO5B[I_HYDRO5B_thresholded[i]])
      }
      # if rounded
      for(i in 1:n_CLD_rounded){
            lower_CLD[i] <- CLD_mes[I_CLD_rounded[i]]-0.005
            upper_CLD[i] <- CLD_mes[I_CLD_rounded[i]]+0.005
```

```
            CLD_bis[I_CLD_rounded[i]]
~dlnorm(CLD_log[I_CLD_rounded[i]],pi_conc_CLD)I(lower_CLD[i],upper_CLD[i])
      }
      for(i in 1:n_HYDRO5B_rounded){
            lower_HYDRO5B[i] <- HYDRO5B_mes[I_HYDRO5B_rounded[i]]-0.005
            upper_HYDRO5B[i] <- HYDRO5B_mes[I_HYDRO5B_rounded[i]]+0.005
            HYDRO5B_bis[I_HYDRO5B_rounded[i]]                                  ~
dlnorm(HYDRO5B_log[I_HYDRO5B_rounded[i]],pi_conc_HYDRO5B)I(lower_HYDRO5B[i]
,upper_HYDRO5B[i])
      }
      # 5b-hydroCLD/CLD mass ratio
      for(i in 1:n){
            ratio[i] ~ dlnorm(ratio_mean_log,pi_ratio)
            ratio_log[i] <- log(ratio[i])
            CLD[i] ~ dlnorm(0,0.0001)
            CLD_log[i] <- log(CLD[i])
            HYDRO5B[i] <- CLD[i]*ratio[i]
            HYDRO5B_log[i] <- log(HYDRO5B[i])
      }
      ratio_mean ~ dlnorm(0,0.0001)
      ratio_mean_log <- log(ratio_mean)
      # standard deviations and precisions
      pi_ratio ~ dgamma(0.001,0.001)
      sd_ratio <- 1/sqrt(pi_ratio)
      sd_conc_CLD <- 0.22
      sd_conc_HYDRO5B <- 0.16
      pi_conc_CLD <- 1/(sd_conc_CLD*sd_conc_CLD)
      pi_conc_HYDRO5B <- 1/(sd_conc_HYDRO5B*sd_conc_HYDRO5B)
}
```

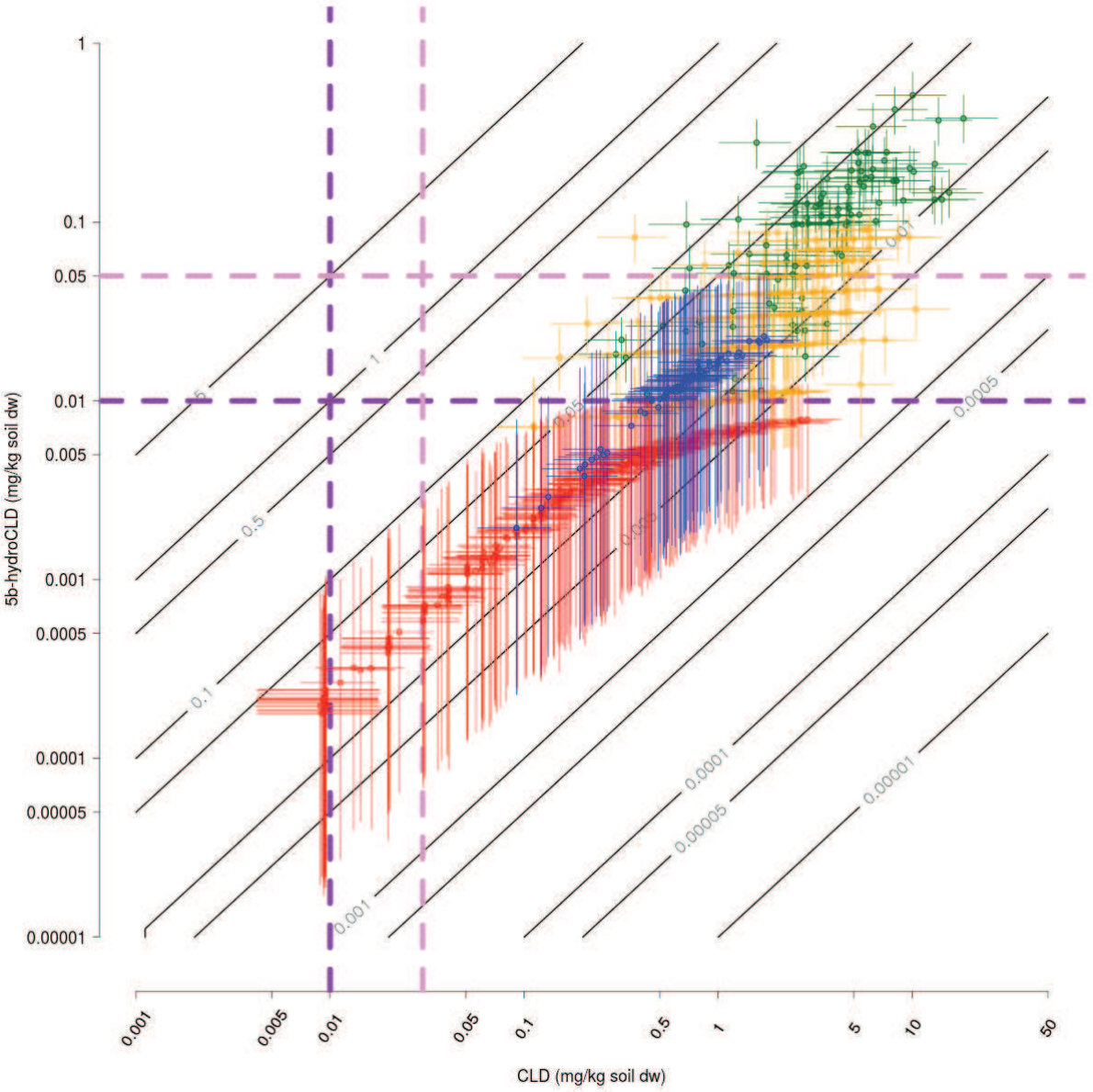

Figure S1: Point (circles) and 95% confidence interval (horizontal lines: CLD; vertical lines: 5b-hydroCLD) estimates for latent 5b-hydroCLD and CLD concentrations in soil computed by the HBM. Concentrations for uncensored data (green) as well as rounded data (orange) and soil samples which measured 5b-hydroCLD concentration were lower than the LOQ (DAAF: red; BRGM: blue) are represented. Oblique black lines are lines of constant 5bhydroCLD/CLD mass ratio. LOQ for CLD and 5b-hydroCLD are plotted as horizontal and vertical dashed lines (DAAF: violet; BRGM: pink).

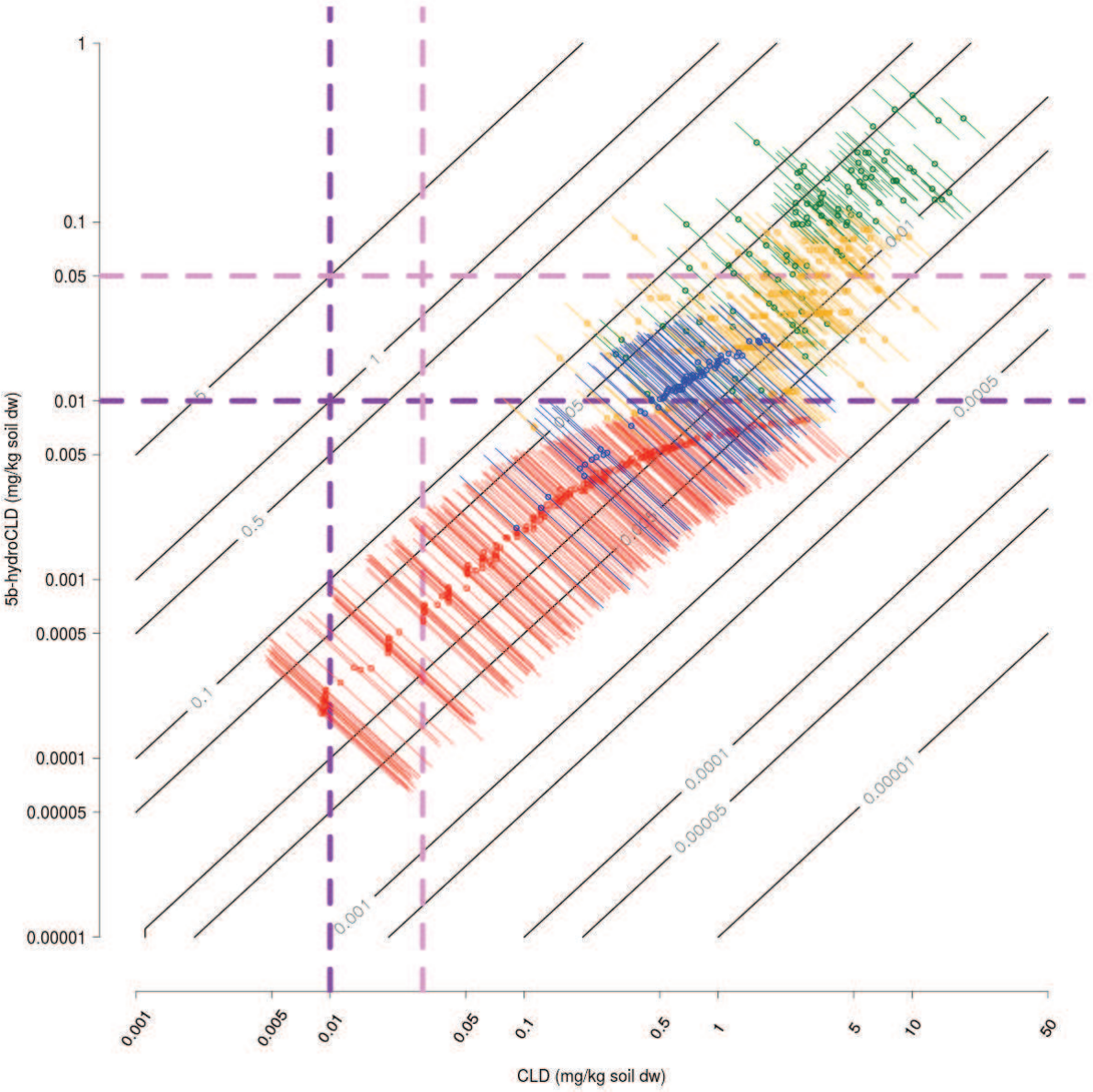

Figure S2: Point estimates for latent 5b-hydroCLD and CLD concentrations (circles) and 95% confidence interval estimates for 5b-hydroCLD/CLD mass ratio (colored oblique lines) in soil computed by the HBM. 5b-hydroCLD/CLD mass ratio for uncensored data (green) as well as rounded data (orange) and soil samples which measured 5b-hydroCLD concentration were lower than the LOQ (DAAF: red; BRGM: blue) are represented. Oblique black lines are lines of constant 5bhydroCLD/CLD mass ratio. LOQ for CLD and 5b-hydroCLD are plotted as horizontal and vertical dashed lines (DAAF: violet; BRGM: pink).

Appendix B – Extraction yields

The extraction yield of both 5b-hydroCLD and CLD were measured in 5 matrices (2 commercial formulations: Curlone-UAG, Curlone-Cirad; 3 soils: Ferralsol, Andosol, Nitisol) with 6 replications (total number of samples: 60). Differences of extraction yields across matrices and across molecules were investigated by applying a two-way ANOVA followed by a LSD pairwise comparison testing procedure. Normality and homoscedasticity of ANOVA residuals were investigated through Shapiro-Wilk and Brown-Forsythe Levene-type tests, respectively.

Inverse of extraction yields were considered in the statistical analysis in order to fulfill ANOVA requirements (Shapiro-Wilk: $p=0.81$; Brown-Forsythe: $p=0.27$). Extraction yields were significantly different across matrices and molecules (ANOVA; matrix: $p=1.03e-09$; molecule: $p=0.86$; interaction matrix x molecule: $p=7.74e-05$).

Extraction yields are plotted (Fig. S3) as box-and-whisker plots (median, upper and lower quartiles, and maximum values). Results of the LSD testing procedure are also represented on the plot (different letters indicate pairwise significant differences at the 5% level). Results of the LSD testing procedure show that extraction yields are similar in the 3 soil matrices and for both molecules (group a). Extraction yields are also similar in the 2 commercial formulations for 5b-hydroCLD (group d) and for CLD (group c). Extraction yields are higher in commercial formulations than in soils for 5b-hydroCLD (groups a-ab VS d) but are similar for CLD (group c).

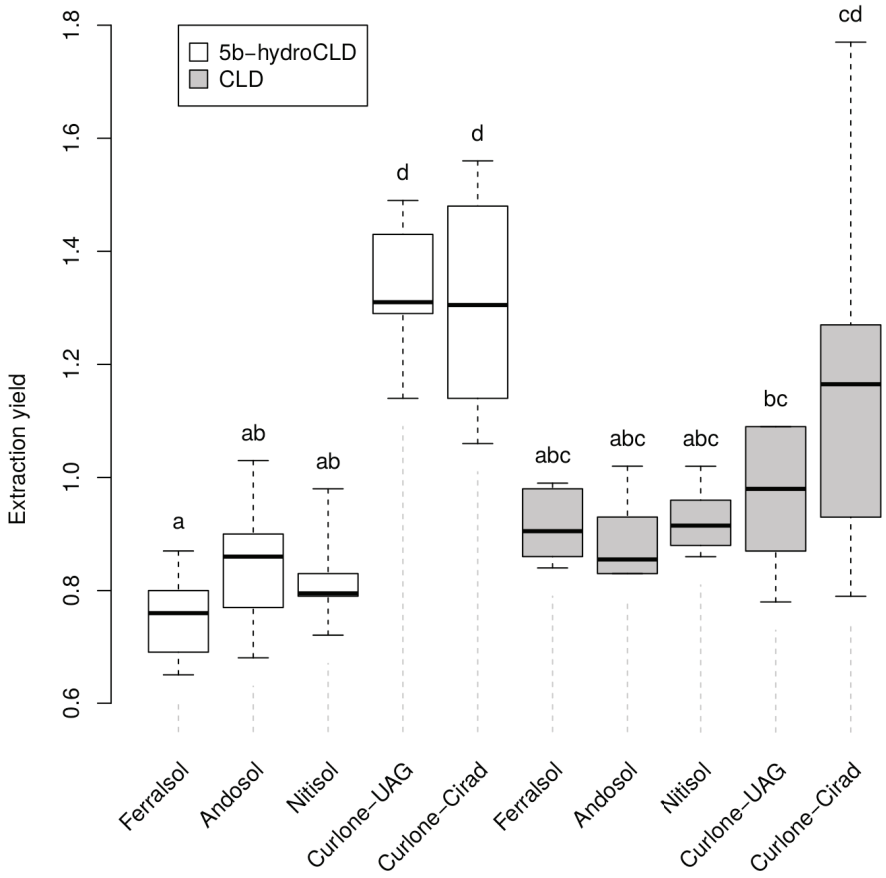

Figure S3

Figure S3. Extraction yields plotted as box-and-whisker plots. (for the explanation of the letter significance above the box see appendix B)